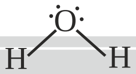
CHAPTER

2

WATER



HYDROGEN BONDING GIVES WATER ITS UNUSUAL PROPERTIES

- Water has high melting point, high boiling point, high heat of vaporization which is a consequence of attraction between adjacent H_2O molecules that give liquid water great internal cohesion.
- Oxygen nucleus attracts electron more strongly than does the hydrogen nucleus as oxygen is more electronegative.
- The result of the unequal electron sharing is two electric dipoles in H_2O molecule, one among each of H bond (each H bears a δ^+) and the oxygen (bears a partial $2\delta^-$).
- Hydrogen bonds are relatively weak.
- Hydrogen bonds are 10% covalent due to overlaps in the bonding orbitals and are 90% electrostatic.
- At room temperature, the thermal energy of an aqueous solution is of the same order of magnitude as that required to break hydrogen bonds.
- The sum of all the hydrogen bonds between water molecules confers great internal cohesion on liquid water.
- Extended networks of hydrogen-bonded water molecules also form bridges between solutes that allow the larger molecules to interact with each other over distances of several nanometres without physically touching.
- Nearly tetrahedral arrangement of the orbitals about the oxygen atom allows each water molecule to form hydrogen bonds with as many as four neighbouring water molecule.
- In liquid water, water molecules are disorganised and in continuous motions, so that each molecule form hydrogen bonds with an average of only 3.4 other molecules whereas in case of ice, each water molecules is fixed in space and forms hydrogen bonds with a full complement of four other water molecule to yield a regular lattice structure.
- During melting or evaporation, entropy of the aqueous system increases.
- At room temperature, both the melting of ice, evaporation of water occurs spontaneously as the tendency of the water molecules to associate through hydrogen bonds is outweighed by the energetic push toward randomness.

WATER FORMS H-BONDS WITH POLAR SOLUTES

- Hydrogen atoms covalently bonded to carbon atoms do not participate in the hydrogen bonding because carbon is only slightly more electronegative than H and thus the C-H bond is only very weakly polar, this is the reason why butanol has a high boiling point (117°C) that butane (-0.5°C).
- Butanol has a polar – OH group and thus can form intermolecular H bonds.
- Uncharged but polar molecules like sugars dissolve readily in water because of the stabilizing effect of hydrogen bonds between – OH group or carbonyl oxygen of sugar and the polar water molecule.
- Hydrogen bonds are strongest when the bonded molecules are oriented to maximise electrostatic interaction, which occurs when the hydrogen atom and the two atoms that share it are in a straight line i.e,. when the acceptor atom is in line with covalent bond between donor atom and hydrogen.

ELECTROSTATIC INTERACTION OF WATER WITH CHARGED SOLUTES

- Water generally dissolves charged or polar compounds.
- Compounds that dissolve easily in water are called hydrophilic (***water loving***).
- Non polar solvents (benzene, toluene) are poor solvents for polar Biomolecules, but they easily dissolve hydrophobic compounds like lipid, waxes.
- NaCl or other salts are easily dissolved in water as water hydrates and stabilizes the Na^+, Cl^- ions by weakening their electrostatic interaction between them and by opposing their tendency to associate together in a crystalline lattice.
- For ionized carboxylic acid, protonated amines, phosphate ester, water easily dissolves them by replacing solute-solute hydrogen bonds with solute-water hydrogen bond, thus screening the electrostatic interaction between them.
- **High Dielectric Constant** of water is mainly responsible for screening the electrostatic interaction between dissolved ions.

  At 25°C, E(dielectric constant) of H_2O – 78.5

  E of benzene (non polar solvent) – 4.6
- Thus ionic interactions between dissolved ions are much stronger in less polar environment.

ENTROPY INCREASES AS CRYSTALLINE SUBSTANCES DISSOLVE

- As salts like NaCl dissolves, Na^+ and Cl^- leaves their crystal lattice and acquires for greater freedom of motion.
- As a result, randomness of the system i.e., entropy increases.
- This increase is largely responsible for dissolving such salt in water.

ΔH - small positive value

$T\Delta S$ - large positive value

$\therefore \ \Delta G$ = negative

Hence, favourable energy change.

NON-POLAR GASES ARE POORLY SOLUBLE IN WATER

- Mostly biological important gases (CO_2, O_2, N_2) are non-polar.
- The movement of the molecules of these gases from the disordered gaseous phase to aqueous solution constrains their motion and motion of water molecules, which leads to decrease in entropy.
- So, reasons for their poor solubility in water

  (i) Non-polar nature.

  (ii) Decrease in entropy when they enter solution.

Note : Three other gases, NH_3, NO, H_2S also have biological roles in some organisms as these gases are polar, dissolves easily in water.

NON-POLAR COMPOUNDS FORCE ENERGETICALLY UNFAVOURABLE CHANGES IN THE STRUCTURE OF WATER

- When water is mixed with non polar solvents neither liquid is soluble in other.
- As they are hydrophobic they are unable to undergo energetically favourable interactions with the hydrogen bonding among water molecules.
- All molecules or ions in aqueous solution interfere with the hydrogen bonding of some water molecules, but polar or charged solutes compensate for lost water-water hydrogen bonds by forming new solute-water interactions.
- So, net change in enthalpy (ΔH) for dissolving these hydrophilic solutes is generally small but hydrophobic solutes, offer no such compensation and their addition to water therefore results in small gain of enthalpy.
- Breaking of hydrogen bonds between water molecules takes up energy from the system, requiring input of energy from surroundings.
- In addition to this requirement of energy, dissolving hydrophobic compounds in water results in measurable decrease in entropy.
- Water molecules in the presence of a non-polar solute are constrained in their possible orientations as they form a highly ordered cage like shell around each solute molecule.
- The number of ordered water molecule, therefore the magnitude of decrease in entropy is directly proportional to the surface area of the hydrophobic solute enclosed within cage of the water molecule.

$$\Delta H = \text{positive},\ \Delta S = \text{negative} \therefore \Delta G = \text{positive}.$$

$$\boxed{\text{Hence, UNFAVOURABLE FREE ENERGY CHANGE}}$$

AMPHIPATHIC COMPOUNDS IN AQUEOUS SOLUTIONS

- These are the compounds which contains both polar (or charged) regions and the non-polar region.
  Ex. Proteins, pigments, certain vitamins, sterols.
- On mixing with water, the polar/hydrophilic region interacts favourably with the solvent and tends to dissolve, but the non-polar/hydrophobic region tends to avoid contact with water.
- The non-polar regions cluster together to present the smallest hydrophobic area to the aqueous solvent and the polar regions are arranged to maximize their interaction with the solvent.
- These stable structure of amphipathic compounds in water are called ***micelles***.
- The force that holds the non-polar regions of the molecules together hydrophobic interactions.
- It's strength is due to the system's achieving greatest thermodynamic stability by minimizing the number of ordered water molecules required to surround hydrophobic portion of the solute molecules.
- Hydrogen bonding between water and polar solutes also causes an ordering of water molecules, but the energetic effect is less significant than that with non-polar solutes.

SOLUTES AFFECT THE COLLIGATIVE PROPERTIES OF AQUEOUS SOLUTION

- Physical properties like vapour pressure, boiling point, melting point (freezing point), osmotic pressure of the solvent, water are called colligative properties (colligative = lied together), because the effect of solutes on all four properties has the same basis –

  "***Concentration of water is lower in solution than in pure water***".
- The effect of solute concentration on the colligative properties of water is independent of the chemical properties of solute, it depends only on the number of solute particles.
- Because the effect of solute on osmolarity depends on the number of dissolved particles, not their mass, macromolecule have therefore less effect on the osmolarity of a solution than would an equal mass of their monomeric components.

NOTE : Plants use osmotic pressure to achieve mechanical rigidity.

IONIZATION OF WATER

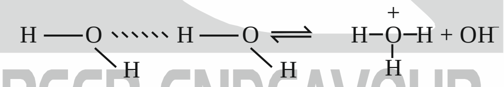
- When weak acids are dissolved in water, they contribute H$^+$ by ionizing, but weak bases consumes H$^+$ by becoming protonated.

PURE WATER IS SLIGHTLY IONIZED

- Water molecules have a slight tendency to undergo reversible ionization of yield hydrogen ion and a hydroxide ion.

$$H_2O \rightleftharpoons H^+ + OH^-$$

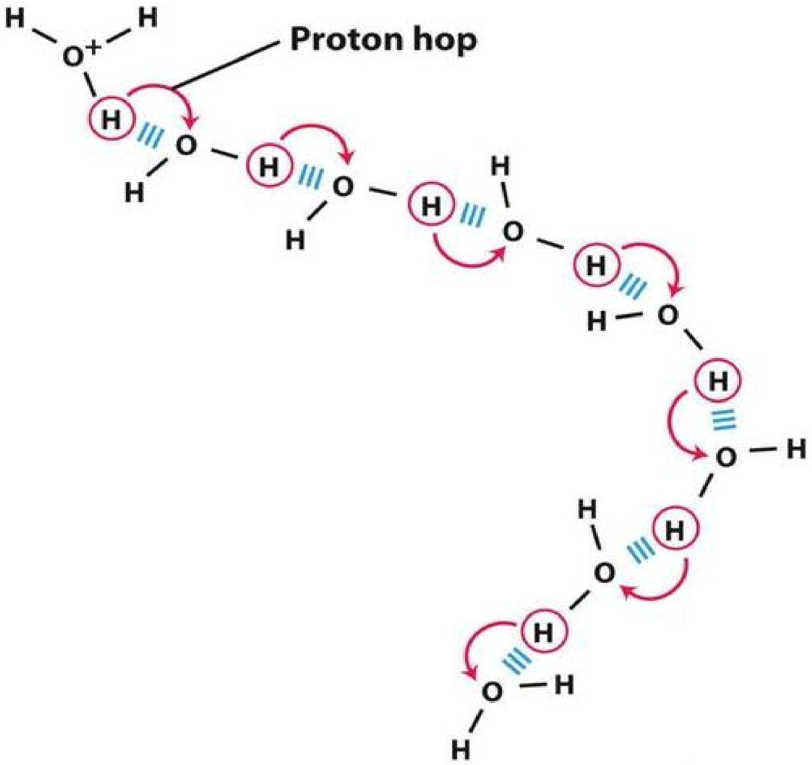
- Free protons do not exist is solution, hydrogen ions formed in water are immediately hydrated to hydronium ions (H_3O^+).



- Pure water carries electrical current as H_3O^+ migrates towards cathode and OH^- migrates towards the anode when a electric field is applied.

1. Movement of H^+, OH^- in electric field is extremely fast compared with that of other ions (Na^+, K^+, Cl^-). Why ??

Soln. The high ionic mobility results from the kind of "proton hoppig". No individual H^+ moves very fast through the bulk solution, but a series of protons hops between the hydrogen bonded water molecules causes the net movement of H^+ over a long distance in a short time.



- Water accepts and becomes   (hydronium ion).
- Same is the reason for high ionic mobility of OH⁻, which also moves rapidly by proton hopping but in opposite direction.

IONIZATION OF WATER IS EXPRESSED BY AN EQUILIBRIUM CONSTANT

$$H_2O \rightleftharpoons H^+ + OH^-$$

- The equilibrium constant for the reversible ionisation of water.

$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]}$$

- In pure water, concentration of water is 55.5 M as the concentration is defined as the gram of H_2O in 1 litre divided by its gram molecular weight $= \frac{1000\,g/L}{18.015\,g/\text{mol}} = 55.5\text{ M}$.

$$\text{Accordingly, } K_{eq} = \frac{[H^+][OH^-]}{[55.5M]}$$

$$\boxed{55.5M \times K_{eq}[H^+][OH^-] = K_w}$$

K_w - Ionic product of water at 25°C.

- Value of K_{eq} , determined by electrical conductivity measurements of pure water is 1.8×10^{-16} M

$$K_w = [H^+][OH^-] = (1.8\times10^{-16}\text{ M})\ (55.5\text{M})$$

$$\boxed{K_w = 1.0\times10^{-14}\text{ M}^2}$$

- Where there are exactly equal concentration of $[H^+],[OH^-]$. As in pure water, the solution is said to be at neutral pH.

  At this pH, concentration H^+, OH^- can be calculated as $K_w = [H^+][OH^-] = [H^+]^2 = [OH^-]^2$

  Solving for $[H^+]$

$$\boxed{[H^+] = \sqrt{K_w} = 10^{-7} M}$$

- As the ion product of water is constant, if $[H^+] >> 1.0\times10^{-7} M$, then $[OH^-]$ must be $<< 1\times10^{-7} M$ and vice – versa.

2. What is the concentration of H^+ in a solution of 0.1 M NaOH ?

$K_w = [H^+][OH^-]$

With $[OH^-]$ = 0.1 M, solving for $[H^+]$ gives

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1\times10^{-14} M^2}{0.1} = 10^{-13}\text{M}$$

3. What is the concentration of OH^- in a solution with an H^+ concentration of $1.3\times10^{-4} M$?

$K_w = [H^+][OH^-]$

With $[H^+]$ = 1.3 × 10^{-4} M

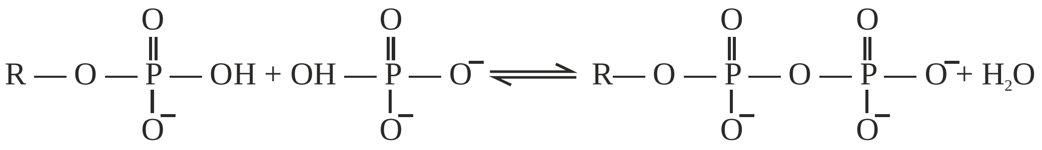
$$[OH^-] = \frac{K_w}{[H^+]}$$

$$[OH^-] = \frac{1.0\times10^{-14} M^2}{1.3\times10^{-4} M}$$

$$[OH^-] = 7.7\times10^{-11} M$$

WATER AS A REACTANT

- Water is not just the solvent in which chemical reaction of living cells occur, it is very often a direct participant in those reactions.



$$R-O-\overset{O}{\overset{\|}{\underset{O^-}{\underset{|}{P}}}}-OH + OH-\overset{O}{\overset{\|}{\underset{O^-}{\underset{|}{P}}}}-O^- \rightleftharpoons R-O-\overset{O}{\overset{\|}{\underset{O^-}{\underset{|}{P}}}}-O-\overset{O}{\overset{\|}{\underset{O^-}{\underset{|}{P}}}}-O^- + H_2O$$

Few examples :

(i) Formation of ATP from ADP + P_i which is an example of condensation reaction in which elements of water are eliminated.

(ii) The reverse of upper one-cleavage accompanied by the addition of the element of water which is a hydrolysis reaction.

- Hydrolysis reaction are also responsible for the enzymatic depolymerisation of proteins, carbohydrates, nucleic acids.

(iii) Water and CO_2 are the end products of oxidation of fuel such as glucose.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

- The metabolic water formed by the oxidation of foods and stored fats is actually enough to allow some animals in very dry habitats to survive for extended periods without drinking water.
- CO_2 produced by glucose oxidation is converted in erythrocytes to more soluble HCO_3^-, in a reaction catalyzed by carbonic anhydrase enzyme.

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

In this reaction, water functions as

(i) Substrate

(ii) In H^+ transfer by forming a network of hydrogen-bonded water molecules through which H^+ hopping occurs.

- Green plants, algae use energy of sunlight to split water in process of photosynthesis.

$$2H_2O + 2A \xrightarrow{\text{light}} O_2 + 2AH_2$$

$A \rightarrow$ electron accepting species varies with organism.

$H_2O \rightarrow$ electron donor in an oxidation reduction sequence that is fundamental to all life.

1. Why is water the 'Universal Solvent" ?

- Water is capable of dissolving a variety of different substances.
- It is called the universal solvent because it dissolves more substances than any other liquid.
- It is water's chemical composition and physical attribute, that make it such an excellent solvent.
- Water molecule have a polar arrangement of the oxygen and hydrogen atoms-one side (H) has a positive electrical charge and the other side (oxygen) has negative change.
- This allow the water molecule to become attracted to many other different types of molecules.

FITNESS OF AN AQUEOUS ENVIRONMENT FOR LIVING ORGANISMS

- The high specific heat of water is useful to cells and organisms because it allows water to act as a heat buffer, keeping the temperature of an organism relatively constant as the temperature of the surrounding fluctuates and as heat is generated as a by product of metabolism.
- Some vertebrates exploit the high heat of vaporization of water by using (thus losing) excess body heat to evaporate sweat.
- The high degree of internal cohesion of liquid water, due to hydrogen bonding is exploited by plants as a means of transporting dissolved nutrients from the roots to the leaves during transpiration.